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(54) **Color film with closely matched acutance between different color records.**

(57) A color photographic silver halide negative working duplicating element comprising a support bearing, in order from the support, at least one red-sensitive photographic silver halide emulsion layer package comprising at least one cyan image-dye forming coupler that is capable upon exposure and processing of forming a cyan image dye that absorbs in the range of the original image; at least one green-sensitive photographic silver halide emulsion layer package comprising at least one magenta image-dye forming coupler that is capable, upon exposure and processing, of forming a magenta image dye that absorbs in the range of the original image; and at least one blue-sensitive photographic silver halide emulsion layer package comprising at least one yellow image-dye forming coupler that is capable upon exposure and processing of forming a yellow image dye that absorbs in the range of the original image. The silver halide particles in the fastest blue sensitive layer have an equivalent spherical diameter no greater than 0.3 microns, while in the remainder of the layers the silver halide particles have an equivalent spherical diameter of no greater than 0.23 microns. The silver level in the fastest blue sensitive layer is no greater than 30 mg/square foot. A sufficient red absorber is present so that the red record MTF(12) is at least 95% of the green record MTF(12) and the red record F50 is no more than 6 cylces/mm less than the green record F50.

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Field of the Invention

This invention relates to a color negative duplicating film in which the red and green records in particular, have closely matched acutance.

Background of the Invention

Color photographic silver halide negative working duplicating elements, especially films, have been known, especially for duplicating color motion picture films. A typical example of such a duplicating element is Eastman Color Intermediate Film manufactured and sold by Eastman Kodak Company, U.S.A. Such a duplicating element is useful in preparing duplicates of motion picture films. The usual construction of such element is to have three records, each record having one or more layers containing emulsions sensitive to different regions of the spectrum, namely the red, green and blue light sensitive layers. Those layers contain color forming compounds which produce cyan, magenta and yellow dyes, respectively, in accordance with the amount of light of red, green and blue colors to which the film is exposed. The records are arranged with the red record lowest (that is, furthest from the light source when the film is exposed in a normal manner), followed by the green record above the red record and the blue record above the green record.

Current practice for most color motion picture production involves the use of at least four photographic steps. The first step is the recording of the scene onto a camera negative photographic film. For applications using two steps this original negative is printed onto a negative working print film, producing a direct print. Most motion picture productions use an additional two steps. The original camera negative film is printed onto a negative working intermediate film, such as the described Eastman Color Intermediate Film, yielding a master positive. The master positive is subsequently printed again onto an intermediate film providing a duplicate negative. Finally, the duplicate negative is printed onto a print film forming the release print. In certain situations, usually involving special effects, the intermediate film may be used four times. In this case, the produced master positive is used to produce a first duplicate negative which is then used to produce a second master positive, which is in turn used to produce a second duplicate negative. The second duplicate negative is used for printing the release print.

Given the number of copies which are made sequentially from the intermediate film it is desirable that the intermediate film produce a negative that enables a print with a minimum degradation in tone scale, color, graininess, and sharpness when compared to the direct print. A known sharpness measurement is acutance. Any sharpness loss (that is, loss in acutance) in the intermediate film will be increased dramatically due to the sequential copying using the intermediate film, as described. Thus, an unacceptable lowering of acutance in the release print as compared to the direct print (which is the most appropriate comparison), may result. Ideally, the intermediate film would produce no degradation of sharpness. In practice, there has always been some sharpness degradation which results in considerable sharpness loss in the sequential copying process described above to produce the release print.

Summary of the Invention

It has been discovered that a significant cause of loss of sharpness in the color negative intermediate film as a whole, is as a result of unequal loss of sharpness in each of the three colored layer sets. In particular, the acutance of the bottom layer in a three color film has always been lower than that of the other two records. This lower acutance of the bottom record occurs because of the light scattering properties of the emulsions in the layers above. Existing intermediate films have the red record on the bottom followed by the green record then the blue record being above the other two records. In particular, the red record, which is typically lowest of the red, green and blue records, tends to suffer the greatest sharpness loss. As a result, when an intermediate film is used to produce release prints, the higher loss of sharpness in the red record becomes highly emphasized during the making of multiple sequential copies to produce the release print. This can cause the resulting release print to exhibit color smudging. It has been discovered that the foregoing loss of sharpness and smudging of the color film as a whole, can be reduced by more closely matching the sharpness loss in the layers (that is, by more closely matching the acutance of the layers). At the same time, excessive sharpness loss in any of the three layer sets can be avoided.

It has been discovered that in a film containing the red, green and blue records in the order described above (that is, red record lowest), that the acutance of the red layer can be markedly increased to a level closer to that of the green record acutance with each layer still having high acutance and without excessive speed loss, by controlling three variables within certain parameters. These variables are the silver halide

particle size of the fastest blue sensitive layer (normally having the largest silver halide particles of all the layers), the silver laydown (sometimes referred to as silver "level" in this application) of the fastest blue-sensitive layer, and the levels of green and red absorbers present (note that a green or red absorbing dye would be colored magenta and cyan, respectively). Preferably, the red record acutance is "closely matched" (as defined later) to that of the green record. In particular, a closer matching of acutance is obtained in a such a film, preferably a color negative duplicating film, when all of the following conditions are satisfied:

1) the silver halide particles in the fastest blue sensitive layer have an equivalent spherical diameter no greater than 0.3 microns, while in the remainder of the layers the silver halide particles have an equivalent spherical diameter of no greater than 0.23 microns;

2) the silver level in the fastest blue sensitive layer is no greater than 323 mg/m^2 (30 mg/ft^2); and

3) a sufficient red absorber is present so that the red record MTF(12) is at least 95% of the green record MTF(12) and the red record F50 is no more than 6 cycles/mm less than the green record F50.

The present invention provides a color photographic silver halide duplicating element according to claim 1. The percentage figures used in this application in comparing MTF(12) values of the red and green absorbers are relative values, thus when it is stated that the red record MTF(12) is at least 95% of the green record MTF(12), this means that the red MTF(12) has a value which is 95% of the value of the green record MTF(12). Likewise, when the red record MTF(12) is stated to be within 5% of the green record MTF-(12), this means within the red record MTF(12) has a value within 5% of the green record MTF(12).

In addition, it is preferred that the red record have an MTF(12) of at least 90% (and more preferably at least 93%) and an F50 of at least 45cycles/mm (and preferably at least 50 cycles/mm).

Detailed Description of Embodiments of the Invention

The first two of the above three factors (that is, silver halide particle size and laydown of fastest blue sensitive layer) is important to control since in all current examples of intermediate films, the fastest blue sensitive layer has the largest silver halide particles of all the light sensitive layers and therefore is typically the most light scattering. Since the fastest blue emulsion causes the most light scattering, the laydown (that is, the amount of silver halide particles) of the emulsion is also important to control. The third parameter described (the amount of absorbers) is important to control since the absorbers absorb and reduce scattered green and red light before they can reach their corresponding light sensitive records. This is particularly important for a red absorber since the red light will tend to be scattered the most when it reaches its corresponding light sensitive record. On the other hand, it is desirable to keep use of light absorbers low since they will typically reduce sensitivity.

It is preferred that color photographic element according to the present invention, have a red record MTF(12) within 5% (more preferably, within 3%) of the green record MTF(12) and the red record F50 within 6 cycles/mm (more preferably within 3 cycles/mm) of the green record F50. It is further preferred that color photographic elements according to the present invention have a silver level in the fastest blue sensitive layer which is no greater than 162 mg/m^2 (15 mg/ft^2). In addition, the red record preferably has an MTF(12) of at least 90% and an F50 of at least 45 cycles/mm.

The above requirements may be applied to any film (positive or negative) having red, green and blue records in the typical order described above. However, a particularly preferred application of the present invention is in negative working color duplicating film.

The silver halide used in the photographic elements of the present invention may be silver bromoiodide, silver bromide, silver chloride, silver chlorobromide, and the like, which are provided in the form of an emulsion. The photographic elements of the present invention preferably use three dimensional emulsions, that is non-tabular grain emulsions. Preferably substantially all of the grains of all of the emulsions are essentially non-tabular grains (that is, at least 90%, preferably 95%, and more preferably about 100%, of the grains are non-tabular). Particularly preferable for the emulsions of all the layers are cubic silver halide emulsions. Tabular silver halide grains are grains having two substantially parallel crystal faces that are larger than any other surface on the grain. Tabular grain emulsions are generally considered to be those in which greater than 50 percent of the total projected area of the emulsion grains are accounted for by tabular grains having a thickness of less than 0.3 μm (0.5 μm for blue sensitive emulsion) and an average tabularity (T) of greater than 25 (preferably greater than 100), where the term "tabularity" is employed in its art recognized usage as

$$T = ECD/t^2$$

where

ECD is the average equivalent circular diameter of the tabular grains in µm and

t is the average thickness in µm of the tabular grains.

The grain size of the silver halide may have any distribution known to be useful in photographic compositions, and may be ether polydipersed or monodispersed, providing it meets the grain size limitations already discussed.

The duplicating element can be processed by compositions and processes known in the photographic art for processing duplicating elements, especially processes and compositions known for preparation of duplicates of motion picture films. A typical example of a useful process is the ECN-2 process of Eastman Kodak Company, U.S.A. and the compositions used in such a process. Such as process and compositions for such a process are described in, for example, "Manual for Processing Eastman Color Films-H-24" available from Eastman Kodak Co. Processing to form a visible dye image includes the step of contacting the exposed element with a color developing agent to reduce developable silver halide and oxidize color developing agent. Oxidized developing agent in turn reacts with the couplers to yield dye. Any color developing agent is useful for processing the described duplicating element. Particularly useful color developing agents are described in, for example, U.S. Patent 4,892,805 in column 17.

The invention is described further in the following Examples.

Example 1

Example 1 describes an experiment which defines the parameters established in this patent. The experiment is a 3 to the third full factorial experiment which involved 27 coatings and used variations shown in Table 1.

Table 1: Parameters Varied in Factorial Experiment

	Low	Medium	High
Fast Blue-Sensitive Emulsion Size* (microns)	0.21	0.26	0.30
Fast Blue-Sensitive Silver Laydowns: (mg/m^2)	151	237	323
Absorber Dye Levels: (mg)			
SMB:	81	113	162
ABS1:	25.3	37.7	39.3

*Emulsion measured by turbidimetric techniques as described in Particle Characterization, vol. 2, pages 14-19, 1985. The measurement yields an equivalent spherical volume/turbidity mean diameter. These measurements will be described here as "equivalent spherical diameters." The cubic emulsions used in this experiment have edge lengths of 0.16, 0.20 and 0.23 microns. Particles having morphologies other than cubic will be related to this measurement by having a volume equivalent to a sphere with the diameter equal to the Esd.

SMB = sulfomethyl blue; also known as 2,6-anthracene disulfonic acid, 9,10-dihydro-1,5-dihydroxy-9,10-dioxo-4,8-bis((sulfomethyl)amino)-4 sodium.

The structure of ABS1 is given below. Both SMB and ABS1 are water soluble and therefore diffuse throughout the multi-layer structure. They also wash out during development.

The above variations were chosen for specific reasons: emulsion sizes larger than the largest size had been shown to be the source of significant light scatter; emulsions smaller than the smallest size seemed unlikely to achieve the speed required for a fast blue emulsion in this system. Fast blue silver laydowns

higher than the highest level were avoided to minimize silver laydown; fast blue silver laydowns lower than the lowest level sacrificed blue layer performance (that is, with larger grains granularity increases significantly and with smaller grains speed is sacrificed). Absorber dye levels higher than the highest level sacrificed too much red-sensitive emulsion speed; absorber dyes lower than the lowest level did not provide sufficient acutance enhancement.

The above variations were coated over a partial multilayer coating consisting of a red-sensitive record, a green sensitive record and with a blue-sensitive record consisting of a mid-blue and slow blue record as follows:

A cellulose acetate film support with a back side Rem jet ™ antihalation layer was coated with the indicated layers, in sequence, with Layer 1 being coated nearest the support. Note that in this Example and in Example 2, when the two red absorber dyes ABS1 and SMB were present together, they were in a ratio of 1 ABS1 to 3SMB by weight (that is, 1/3 by weight). Coverages in parentheses are milligrams per meter squared, unless otherwise indicated).

Layer Arrangement

Layer 1: Slow Cyan
0.288 g/m^2 of a red sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion with an edge length of 0.042 µm and chemically sensitized with sulfur and gold sensitizers.
0.347 g/m^2 of cyan image-dye forming coupler C-1.
0.072 g/m^2 of masking coupler MC-1.
0.031 g/m^2 of cyan absorber dyes ABS1 and SMB.
3.068 g/m^2 of gelatin vehicle.

Layer 2: Mid cyan
0.187 g/m^2 of a red sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion with an edge length of 0.072 µm and chemically sensitized with sulfur and gold sensitizers.
0.161 g/m^2 of cyan image-dye forming coupler C-1.
0.052 g/m^2 of masking coupler MC-1.
0.023 g/m^2 of cyan absorber dyes ABS1 and SMB.
0.727 g/m^2 of gelatin vehicle.

Layer 3: Fast cyan
0.230 g/m^2 of 50% by weight red sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion with an edge length of 0.136 µm and chemically sensitized with sulfur and gold sensitizers with 50% by weight red sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion with an edge length of 0.091 µm and chemically sensitized with sulfur and gold sensitizers
0.114 g/m^2 of cyan image-dye forming coupler C-1.
0.005 g/m^2 of masking coupler MC-1.
0.027 g/m^2 of cyan absorber dyes ABS1 and SMB.
0.807 g/m^2 of gelatin vehicle.

Layer 4: Interlayer
0.700 g/m^2 of gelatin vehicle.
0.269 g/m^2 of DOX-1.

Layer 5: Slow Magenta
0.389 g/m^2 of green sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion with an edge length of 0.056 µm and chemically sensitized with sulfur and gold sensitizers.
0.329 g/m^2 of magenta image-dye forming coupler M-1.
0.104 g/m^2 of masking coupler MC-2.
0.015 g/m^2 of magenta absorber dye 4,5-dihydroxy-3-(6',8'-disulfo-2'-naptho azo)-2,7-napthalene disulfonic acid tetrasodium salt (ABS2).
2.530 g/m^2 of gelatin vehicle.

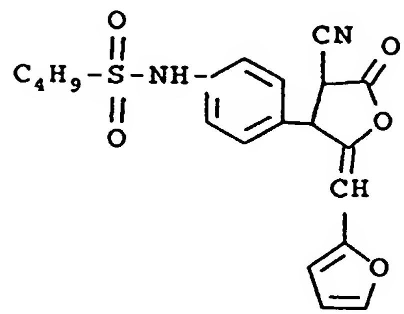
Layer 6: Mid Magenta
0.217 g/m^2 of green sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion with an edge length of 0.080 µm and chemically sensitized with sulfur and gold sensitizers.
0.140 g/m^2 of magenta image-dye forming coupler M-1.
0.073 g/m^2 of masking coupler MC-2.
0.014 g/m^2 of magenta absorber dye ABS2.
0.727 g/m^2 of gelatin vehicle.

Layer 7: Fast Magenta
0.271 g/m^2 of green sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion with an edge length of 0.115 μm and chemically sensitized with sulfur and gold sensitizers.
0.029 g/m^2 of magenta image-dye forming coupler M-1.
1.051 g/m^2 of magenta image-dye forming coupler M-2.
0.014 g/m^2 of masking coupler MC-2.
0.024 g/m^2 of magenta absorber dye ABS2.
0.727 g/m^2 of gelatin vehicle.

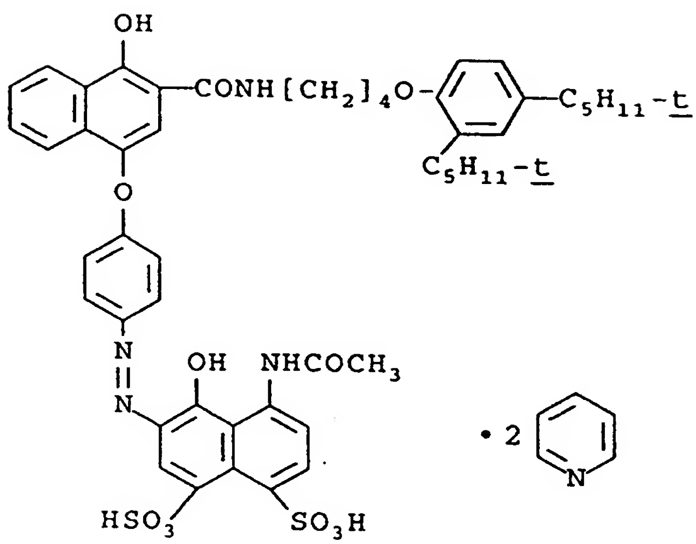
Layer 8: Interlayer
0.700 g/m^2 of gelatin vehicle.
0.269 g/m^2 of DOX-1
0.065 g/m^2 of yellow filter dye Y-1.

Layer 9: Slow Yellow
(227 as Ag) 30% by weight blue sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion, 0.115 micron grain size chemically sensitized with sulfur and gold chemical sensitizers and containing blue spectral sensitizers; with 70% by weight blue sensitized cubic grain silver bromoiodide emulsion 0.091 micron grain size;
(803) yellow image dye forming coupler Y-1;
(22) the magenta color masking coupler MC-3 shown in Example 2 below.
(16) cyan coupler c-1
(2313) gelatin vehicle

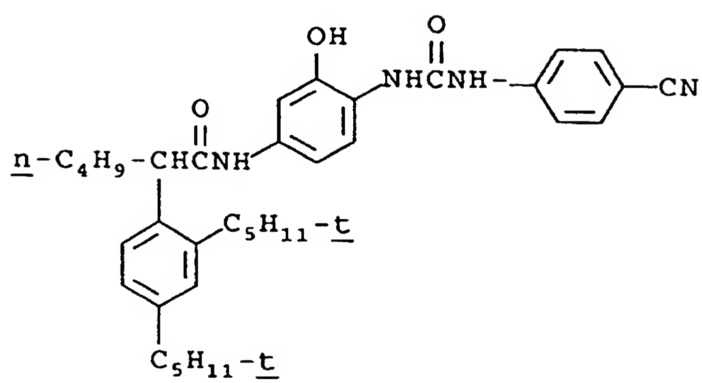
Layer 10: Mid Yellow
(162 as Ag) Blue sensitized cubic grain silver bromoiodide (3.5% iodide) emulsion, 0.145 micron grain size chemically sensitized with sulfur and gold chemical sensitzers and containing red spectral sensitizer.
(222) yellow image-dye forming coupler Y-1.
(11) the magenta colored masking coupler MC-3 shown in Example 2 below.
(8) cyan coupler C-1.
(699) gelatin vehicle.



Y-1

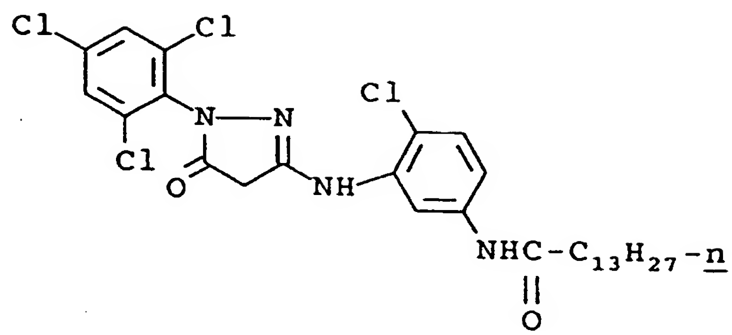


MC-1

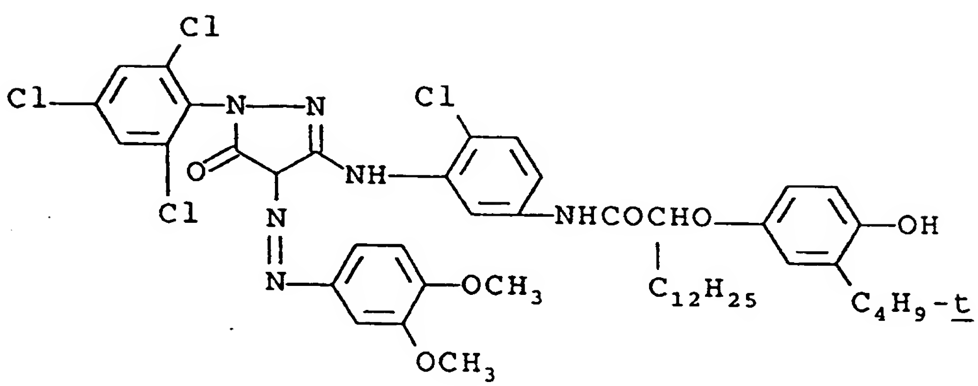


C-1

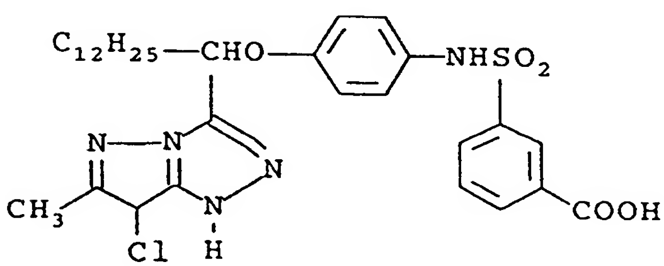
didodecylhydroquinone DOX-1



M-1

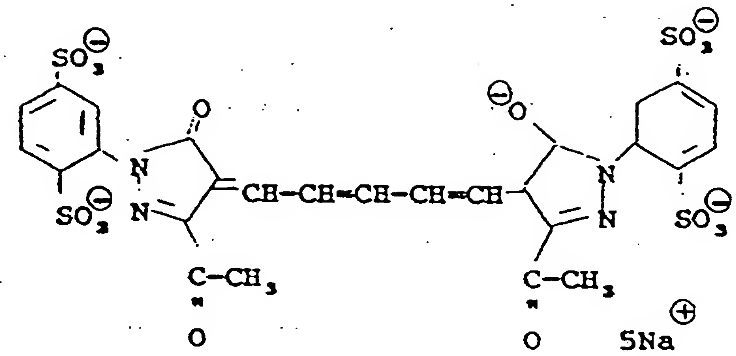


MC-2



M-2

Bis[3-acetyl-1-(2,5-disulfophenyl)-2-pyrazolin-5-one-(4)]-pentamethine oxonol, pentasodium salt



ABS 1

The coatings were given MTF separation exposures. The separation exposures produced exposure in one light senstive layer at a time. Separation exposures were used to eliminate the influence of interlayer interimage effects on acutance. The input exposure modulation was 60 percent. The strips were processed in the ECN-2 process. Resulting images were evaluated to generate standard red, green and blue MTF curves.

For purposes of quantifying acutance, two parameters were derived from the MTF curves: these two parameters were used in order to characterize both the low frequency region and the high frequency region of the curves. The MTF at 12 cycles per mm , MTF(12), was chosen to be an appropriate descriptor of the low frequency response. The frequency at which the MTF equals 50 percent (F50) was chosen to be an appropriate descriptor of high frequency response. These parameters, MTF(12) and F50 were then modeled using standard linear regression techniques to provide responses as a function of the experimental parameters. Such a model provides estimations of the responses for combinations of parameters in addition to those actually tested.

There are two parts to the foregoing effort; the first is identification of the conditions required to ensure high red acutance, and the second is to identifiy the conditions required for closely matched acutance between the green and red MTF. Overlap between these two parts yields conditions which give both high red acutance and closely matched red and green acutance..

High Red Acutance

For the purposes of this example, high red acutance is defined to correspond to an MTF(12) of greater than 93 percent and and F50 of greater than 50 cycles. The linear regression for MTF(12) was used to generate the cyan dye levels required to achieve an MTF(12) of greater than 93 percent for 5 grain sizes and 5 fast blue silver laydowns. These are shown in Table 2.

Table 2

Red Absorber Dye Levels Required to Achieve MTF(12) Greater Than 93 Percent (absorber dye level of smb in mg/m2, ABS1 was at 1/3 smb level in each case)						
		Fast Yellow Silver Laydown (mg/sq meter)				
		151	192	237	282	323
Fast Yellow Emulsion Size (in microns, equivalent spherical diameter)	0.21	>85	>93	>100	>98	>95
	0.235	>88	>95	>105	>103	>98
	0.26	>88	>98	>108	>108	>103
	0.28	>88	>98	>108	>110	>105
	0.30	>88	>98	>108	>110	>108

Table 2 shows that the lower frequency MTF goal, as quantified by MTF(12) greater than 93 percent, can be achieved with virtually all of the combinations of grain size and silver laydown in the Table, although the higher levels of silver laydown, and the larger grain sizes require some increase in absorber dye levels. Similarly, the linear regression for F50 was used to generate cyan (that is, red absorber) dye levels required to achieve F50 of greater than 50 cycles/mm. That operation yields Table 3.

Table 3

Red Absorber Dye Levels Required to Achieve F50 Greater Than 50 cycles/mm (absorber dye level of smb in mg/m2, ABS1 was at 1/3 smb level in each case)						
		Fast Yellow Silver Laydown (mg/sq meter)				
		151	192	237	282	323
Fast Yellow Emulsion Size (in microns, equivalent spherical diameter)	0.21	all	all	>85	>90	>93
	0.235	all	all	>93	>100	>103
	0.26	all	all	>103	>113	>118
	0.28	all	all	>113	>131	>136
	0.30	all	all	>133	n/a	n/a
"all" indicates that all dye levels within the range of the experiment provided required performance (that is F50 > 50 cycles/mm) n/a indicates that dye levels within the range of the experiment did not provide required performance						

Table 3 illustrates the immense effect of silver laydown levels on light scatter. At the lower silver laydowns, all dye levels within the range of the experiment can achieve an F50 of 50 cycles/mm. At the higher silver laydown levels and larger grain sizes, none of the dye levels within the range of the experiment can achieve an F50 of 50.

In order to satisfy the high red acutance requirement, both the conditions in Table 2 and the conditions in Table 3 should be satisfied concurrently. Thus the more restrictive condition from each table may be combined to yield another table which indicates the dye levels required to simultaneously achieve an MTF-(12) greater than 93 percent and an F50 higher than 50 cycles/mm. The combination of those two tables is shown in Table 4.